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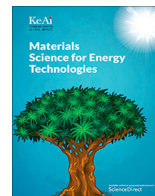
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Bismuth-nanoparticles decorated multi-wall-carbon-nanotubes cast-coated on carbon paste electrode; an electrochemical sensor for sensitive determination of Gallic Acid at neutral pH

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ABSTRACT

In this work, we have successfully developed a novel amperometric sensor for the detection of Gallic Acid (GA) based on bismuth nanoparticles decorated multi-wall-carbon-nanotubes modified carbon paste electrode (Bi-MWCNT/MCPE) at physiological pH. We investigated electrochemical oxidation of GA at neutral pH since there is limited literature at this pH. Surface morphology of the synthesized Bi-MWCNT composite was examined using high resolution transmission electron microscopy (TEM) and X-ray diffraction (XRD). Our fabricated Bi-MWCNT/MCPE was characterized with the aid of field emission scanning electron microscopy (FE-SEM) coupled to energy dispersive X-ray (EDX). The electron impedance spectroscopy (EIS) was employed to study the electrode–electrolyte interface properties, which depicted least electron transfer at Bi-MWCNT/MCPE. During Cyclic voltammetric (CV) analysis of GA at Bi-MWCNT/MCPE, we observed a threefold enhancement in anodic peak current (I_{pa}) compared to bare CPE. Amperometric quantitative analysis implied proportionality between I_{pa} and GA concentration in the range 1.0 to 100.0 μM with the lower detection limit (LOD) of $1.6 \times 10^{-7} \text{ M}$ ($S/N = 3.3$). Results from the interference study indicated good anti-interference property of the proposed sensor and could as well be subjected for real sample analysis, which was fortifying with GA. From the acceptable recoveries obtained we confirm the sensor's practical applicability. Finally, the developed sensor offered many benefits such as excellent detection particularly at neutral pH, wide linear dynamic range, selectivity, stability, and reproducibility.

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1. Introduction

GA (Scheme 1) is a naturally available antioxidant [1]. It is an omnipresent compound found in green tea, fruits and vegetables. GA is reported to possess properties such as antioxidant [2], antiviral, antibacterial, anti-diabetic, anti-cancer, anti-aging, and anti-inflammatory properties [3]. Apart from those, it has many healing benefits in diseases such as cardiovascular, neuro-degenerative, and towards aging. It was found to show cytotoxic effects against

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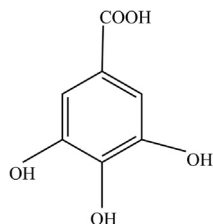
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cancer cells without harming normal cells [4,5]. In its structure it possesses phenolic group which can delocalize free radicals produced over it [6]. Hence, it acts as a universal scavenger, capable of deactivating reactive oxygen species and reactive nitrogen species by donating an electron at neutral pH [7]. GA sensor has many large scale industrial applications. GA is often used as an indicator for the authenticity of fruit juices and many different alcoholic beverages. In recent years, GA was illegally added into fake liquors to make adulteration [8]. The therapeutic effect of GA could be assessed by measuring its concentration in body fluids. Therefore, the quantitative determination of GA concentration in food, human fluids and medicinal plants could be used to develop biology, pharmacological research and life sciences. As GA is a polyphenolic acid it is used as a standard for the determination of phenolic content by Folin-Ciocalteu assay. Besides these it is also used in dyes, photography and printing inks industries. It prevents the rancidity of food and spoilage of fats and oils due to its antioxidant nature



Scheme 1. Structure of Gallic Acid.

enabling its application as food additives in various food products such as baked goods, chewing gums and candy. Owing to its UV shielding ability it can be used in cosmetics [9]. Recent reports have displayed antibacterial property of GA against a wide range of pathogens which included *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Klebsiella pneumonia*. Hence determination of GA can be used in several of these applications.

Tea is a common beverage which contains a lot of antioxidants and GA being one of them. Therefore, its routine consumption must be encouraged in order to benefit from its therapeutic properties. Hence it becomes a likely target for the determination of GA. On account of its biological importance, pharmaceutical and industrial applications, determination of GA in real samples by developing a simple, rapid, cost effective, and sensitive method is necessary. From recent studies, it is known that among spices, clove also contains GA [10]. Therefore, we chose to use clove too for real sample analysis as this hasn't been reported in literature so far.

After an extensive literature survey, we found out that several analytical techniques have been used for the determination of GA. These methods include HPLC [11,12], Gas Chromatography, liquid Chromatography [13,14], flow injection analysis [15], spectrophotometry [16], photo electrochemical methods [17], etc. However, these methods involve expensive instrumentations, burdensome procedures, intricate sample preparations, etc [18]. Thus, these methods are not favored for on-site real time sampling and during routine analysis of GA. Since GA is an electro-active compound electro-analytical techniques such as voltammetry, can be easily employed for its determination [19]. Of the various working electrodes available, in our work we have used carbon paste electrodes [20,21] as it offers various benefits such as its amenability for modification, quick regenerative surface, low background current, wide potential window, low ohmic resistance and most of all cost effectiveness [22–24].

This is the era of nanomaterials and currently a great deal of research has been focused on developing nanomaterials due to its signal amplification in electrochemical sensors [25]. Various nano-materials have been studied for different purposes [26]. They have a larger surface area for biomolecules to be immobilized thereby increasing the number of binding sites available for the detection of a specific analyte. Various types of nanomaterials are used in electrochemical sensors [27]. Amongst all, carbon nanotubes (CNT) [28] and their composites strike as the most remarkable and versatile materials. They are composed of sp^2 carbon atoms oriented as one (CNT) or multiple concentric tubes (MWCNT). The latter has gained more importance owing to its higher yield, low cost of production, physiochemical properties thermo-chemical stability and finally the ability to maintain or improve its excellent electrical properties when subjected to different functionalization processes [29]. MWCNT also present extraordinary active surface area, chemical inertness, high strength, good conductivity properties and low charge-transfer resistance in solutions [30]. The use of new and innovative materials for modifying MWCNT and its composites based sensors has

gained tremendous significance in the field of pharmaceutical industry and environmental research [31,32]. Hence, we have utilized MWCNT in the present work for detecting GA. Bi-nanoparticles are known for their eminent selective sensing; possess a large specific surface area and is biocompatible [33,34]. They have unique physical and chemical properties such as high electro catalytic activity, higher surface free energy and good conductivity which favor absorption of GA [35]. In order to utilize their properties imperiously we synthesized Bi-MWCNT nano composite and successfully applied it as an efficient modifier on CPE.

Our results portray Bi-MWCNT as an excellent platform with large specific surface area that offered least charge transfer resistance for GA electro-oxidation. Bi-MWCNT dispersion was drop coated on bare CPE. For best performance of our Bi-MWCNT/MCPE, we optimized conditions such as pH and volume of Bi-MWCNT casting. In conclusion we have presented a sensitive and selective method for amperometric evaluation of GA based on its oxidation signal at neutral pH using environmentally friendly sensor which is cost effective. Finally we have demonstrated the practical applicability of our fabricated sensor in real samples such as green tea and clove extracts by obtaining the satisfactory recovery values.

2. Experimental

2.1. Reagents

GA was procured from TCI (Japan). Ascorbic Acid (AA), KH_2PO_4 , NaOH pellets, H_3PO_4 , Dimethyl formamide (DMF) and silicone oil were all from Merck (India). Graphite powder was procured from Graphite India Pvt. Limited (India). All reagents were of analytical grade and used as procured. All aqueous solutions were solutions were prepared using ultrapure water (resistivity $>18.2 \text{ M}\Omega\text{cm}$) from Milli-Q Plus system (Millipore). KH_2PO_4 and NaOH stock solutions were used to prepare phosphate buffer (PBS) pH (2.0–8.0) and the pH of the solution was adjusted using either H_3PO_4 or NaOH. Stock solution of $1 \times 10^{-3} \text{ M}$ of GA was prepared in ultrapure water. Pristine-MWCNT (p-MWCNT) was procured from Laboratory of chemistry and electrochemistry surfaces, University of Namur, Belgium. conc. H_2SO_4 , conc. HNO_3 , and Bismuth salt (of Merck make).

2.2. Instrumentation and apparatus

All the electrochemical studies were performed using EA-201 Electro Analyzer Chemi-Link system (India). A standard three electrode system was used for all the electrochemical studies, which comprised of a bare or modified electrode as the working electrode, a platinum electrode as auxiliary electrode and saturated calomel electrode as a reference electrode. The surface morphology of the electrode was studied using FE-SEM (JSM-7500F) and an EDX spectrum was used to obtain elemental composition of the electrodes materials. The measurement of pH of the buffer solutions was done using a digital pH/mV meter ELICO Li 614 (India). HRTEM and XRD studies were carried out using TECNAI G² 20 LaB6 and PAN analytical Xpert PRO Bragg-Brentano diffractometer at an operating voltage of 45 kV and tube current of 30 mA with Cu K α .

2.3. Preparations of the bare and modified CPE

The ratio of graphite powder to silicone oil (binder) was optimized for best results. Bare CPE was prepared by thoroughly grinding graphite powder with silicone oil in the ratio 70:30 (wt/wt %) in a mortar and pestle for an hour till a homogenous paste was obtained. This homogenous paste was then filled into a cavity of

the Teflon tube and smoothened to obtain a smooth and crack free surface. Next for the preparation of modified electrode, 2.0 mg of the Bi-MWCNT taken in 1.0 ml of DMF was sonicated for 30 min. 4.0 μL of this suspension was drop-cast onto the bare CPE surface. This was then followed by, blow drying for 6.0 min to evaporate the solvent. This electrode was then denoted as Bi-MWCNT/MCPE. For control study we used p-MWCNT, similarly 4.0 μL was cast coated on CPE denoted as p-MWCNT/MCPE.

2.4. Synthesis of Bi-MWCNT nano-composite

1.0 g of crude (pristine) MWCNTs was placed in a 500 ml round bottomed flask containing a mixture of 75 ml conc. H_2SO_4 (96%) + 25 ml conc. HNO_3 (65%). This mixture was magnetically stirred and subjected to refluxing (using an oil bath) for 6 h at 50 $^\circ\text{C}$. Afterwards, the mixture was allowed to attain room temperature. It was then transferred to a beaker containing Milli-Q water, which was then filtered and its residue was washed several times with de-ionized water until neutral pH was attained. The above oxidized MWCNTs was mixed with the bismuth salt aqueous solution and then subjected to sonication for 10 min using an ultrasonic tip. This was followed by IR irradiation for 2 h. Then the mixture was cooled down to room temperature, filtered and washed with water and dried in air. Finally, this was calcined under continuous flow of argon gas to get Bi nanoparticles decorated MWCNTs.

2.5. Real sample preparations

Few cloves were taken and crushed using mortar and pestle, which was then dissolved in distilled water and filtered to remove solid particles. This filtrate was then diluted and used for GA estimation. Another real sample which was chosen was green tea sample (Darjeeling green tea sachets). One green tea sachet was immersed in 200 ml hot water for 10 min for extraction. Then 5 ml of this extract was used for GA estimation.

3. Results and discussion

3.1. Characterization of synthesized Bi-MWCNT composite using HRTEM

Fig. 1(a) shows the HR-TEM image of Bi-MWCNT composite taken on a carbon-coated copper grid. It portrays the nano tubular structure of MWCNT and the dark spots on the MWCNT correspond to the presence of Bi-nanoparticles strongly anchored and evenly distributed onto MWCNT, as we do not find any free Bi- particles away from the tube. It is common to see Bismuth nano particles in its oxide form as nano-particles are very reactive and it gets slowly oxidized. PXRD patterns in Fig. 1(b) revealed the presence of Bi nanoparticles and also sharp peaks indicate that the particles are crystalline in nature [36,37].

3.2. Characterization of modified electrodes by FE-SEM and EDX

The surface morphology of CPE and Bi-MWCNT/MCPE was characterized by recording the FE-SEM images as shown in Fig. 2(a) and (b) respectively. The FE-SEM image of bare CPE displays a typical flake like structure of graphite. However, in the FE-SEM image of Bi-MWCNT/MCPE, we witnessed Bi-MWCNT composite covering the entire CPE surface because of the employed casting method. Small Bi nanoparticles are definitely seen on the MWCNT surface. This is further confirmed from the FE-SEM image in LABE mode (Low-angle back scattered electron) in Fig. 2(c). In this mode, higher atomic element appears brighter than the lower atomic element. As bismuth has very high atomic number, the brighter part

in the figure corresponds to bismuth and the darker part represents the other elements. The small sized bismuth nanoparticles are homogeneously distributed on the surface. Although there is one bigger particle present, this may have resulted from the agglomeration of nanoparticles which is comparatively very few in numbers. We used EDX to determine the elemental composition of Bi-MWCNT-MCPE composite. As represented in Fig. 2(d) atomic percentages of the elements: carbon, oxygen, silicon and bismuth were present in the ratio 93.0, 5.08, 0.50 and 1.43 respectively. This confirms the existence of Bi in the composite.

3.3. Electrochemical characterization

Electrode reaction rates and most double layer parameters are extensive quantities and always have to be referred to the unit area of the interface. Knowledge of the real surface area of electrodes is therefore very much required. In order to measure the electrochemically active surface areas of the prepared electrode, CV was performed using the classical redox system of potassium ferri-cyanide ($0.1 \times 10^{-3} \text{ M}$) in KNO_3 (1.0 M). The total effective electrode surface area was calculated by Randle-Sevick equation [38];

$$I_{pa} = (2.69 \times 10^5) n^{3/2} ACD^{1/2} \nu^{1/2} \quad (1)$$

Here n is the number of electrons in the redox reaction, A is the area of working electrode, D is the diffusion coefficient for the electro-active species, ν is the scan rate, and C is the concentration of the electro-active species at the electrode. On substituting the values, the area of CPE and Bi-MWCNT/MCPE were found to be 0.047 cm^2 and 0.090 cm^2 respectively. A 1.9 times increase in surface area was observed upon modification. This increase in the surface area also contributed towards the increment in current.

Electrochemical impedance spectroscopy is an effective tool to study the properties of electrode/solution interface and the ease with which charge transfer occurs between the solution containing the analyte and electrode interface. Fig. 3(a) illustrates the Nyquist plot CPE and Bi-MWCNT/MCPE. The EIS data of the electrodes were obtained in AC frequency range varying from 0.1 Hz and 100 kHz at the oxidation peak potential. Charge transfer resistance (R_{ct}) values were obtained after fitting the impedance data to Randles equivalent circuit as shown in Fig. 3(a) inset. R_s represents uncompensated resistance due to electrolyte, R_{ct} is charge transfer resistance, C_{dl} is double layer capacitance and W is Warburg impedance. The R_{ct} values for CPE and Bi-MWCNT/MCPE were $12.4 \times 10^3 \Omega$ and $8.76 \times 10^3 \Omega$ respectively. Least R_{ct} offered at Bi-MWCNTs/MCPE implies that it facilitates subtle electron transfer at Bi-MWCNT/MCPE compared to CPE. Hence Bi-MWCNT/MCPE was found to be very efficient for the development of electrochemical sensor for GA.

3.4. Effect of variation of casting volumes of Bi-MWCNTs on the carbon paste matrix

The amount of modifier plays an important role towards the sensitivity of the proposed sensor. Fig. S1 (Supplementary information) shows the effect of Bi-MWCNT composite casting volume upon GA anodic peak current response. Casting volumes from 2.0 to 6.0 μL were varied. We observed that the anodic peak current increased with increasing cast volume, which can be attributed to the increase in surface area of Bi-MWCNT. With a casting volume of 2.0 μL , the electrode surface was not completely covered. However at 3.0 μL , although it covered the surface, current magnification was not that great. Beyond 5.0 μL , though the peak current increased tremendously, it was accompanied with a shift in potential indicating higher activation energy for oxidation which was not a favorable response. Also casting 6.0 μL of Bi-MWCNT onto

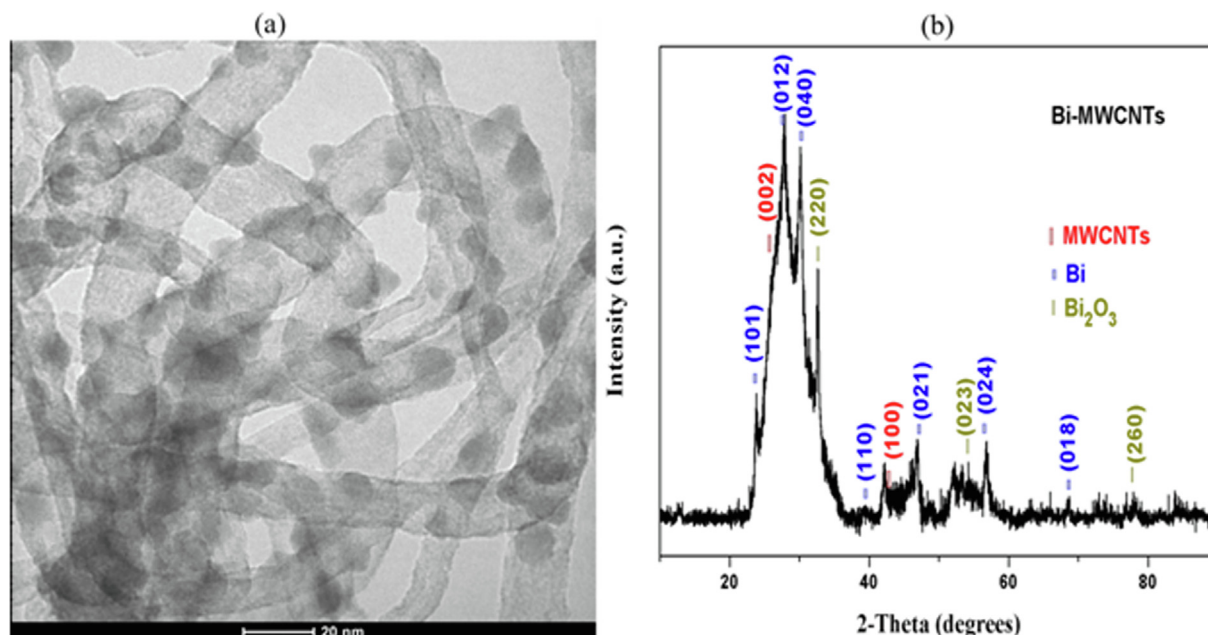


Fig. 1. (a) HR-TEM image, and (b) PXRD patterns of Bi-MWCNT.

the surface, we observed that the suspension overflowed from the CPE surface hampering reproducibility due to uneven surface. Hence an optimum cast volume of 4.0 μL of Bi-MWCNT was used for further experiments for optimum current magnifications.

3.5. Electrochemical behavior of GA at Bi-MWCNT/MCPE

CV technique was employed to investigate the electrochemical behavior of GA at Bi-MWCNT/MCPE. Cyclic voltammograms observed at CPE and MCPE for 1×10^{-3} M GA in 0.1 M phosphate buffer at pH 7.0 is displayed in Fig. 3(b). At both the electrodes, we observed the appearance of anodic peaks and the absence of their reduction counter parts indicating the process to be totally irreversible. The observed anodic currents at bare CPE and Bi-MWCNT/MCPE were 35.0 μA (233 mV) and 108.3 μA (280 mV) respectively. Low current at CPE is due to sluggish electron transfer. Further, we performed control study to establish the superiority of Bi-MWCNT/MCPE, using p-MWCNT/MCPE. We observed that p-MWCNT produced poor response for GA electro-oxidation. The anodic current response for GA at p-MWCNT/MCPE was 43.0 μA which was only a substantial increase compared to that at Bi-MWCNT/MCPE. This can be well justified on the basis of poor dispersing ability of p-MWCNT to make a good suspension and also upon cast coating on CPE the suspension did not completely cover the surface. These results indicated the significance of Bi-nanoparticles in MWCNT matrix to be the major reason behind the improved sensitivity for GA detection. Bi nano-particles have excellent electrochemical characteristics such as large superficial area and intensification of contribution in radial mass transport. The thus formed nano-composite of Bi-MWCNT is an interesting material due to its synergistic effect that resulted in enhanced anodic current for GA [39]. Hence, a threefold increment in anodic peak current upon modification was observed. The aromatic ring system of GA may involve in π - π stacking with Bi-MWCNT which is responsible in facilitating the facile electron transfer. Also the ability of MWCNT to facilitate high electron transfer kinetics contributed favorably to the enhancement in current. The increase in surface area and excellent conductivity of Bi-MWCNTs also played a predominant role in the increment in current. Hence these results

indicated our sensor to be sensitive and hence can very well be used for GA quantification.

3.6. Effect of buffer pH

pH is one of the most important aspect, which plays a crucial role in the electrochemical response of GA. The effect of variation of pH on 1×10^{-3} M GA was studied using CV technique in 0.1 M PBS, pH in the range 2.0–8.0. The results are depicted in Fig. S2 (Supplementary information). The variations of I_{pa} and E_{pa} with pH respectively are displayed in Fig. 4. From Fig. 4(a) it was observed that the I_{pa} decreased with increase in pH between 2.0 and 6.0 with a slight increase at pH 7.0 and then a steep decrease further. Hence it could be concluded that the protons could catalyze the electrochemical oxidation of GA. On increasing the pH from 2.0 to 8.0, the protonated degree of GA decreases, thus the static attraction between GA and Bi-MWCNT decreases upon going towards basic pH. But at pH 7.0 there is a slight jump in anodic peak current. After thorough literature survey, it was observed that GA has not been much studied at neutral pH. Hence, we examined GA electrochemical response at neutral pH and the same pH was used for all other experiments.

The peak potentials E_{pa} shifted towards negative potential with increase in pH as shown in Fig. 4(b) suggesting the involvement of protons. The least square treatment of the calibration graph yielded the following regression equation: $E_{pa} = 571.27 - 38.42 \text{ pH}$ and $R^2 = 0.9441$. The slope of 38.42 mV/pH denotes an inequality in the number of protons and electrons in the oxidation of GA. The decrease in the slope as compared to the theoretical value of 59 mV/pH, suggests a $2e^-/1H^+$ transfer process [40,41].

3.7. Effect of scan rate variation

The variation of scan rate on I_{pa} of GA was studied at Bi-MWCNT/MCPE. CV with varying scan rates (25–125 mV) was performed in a solution containing 1×10^{-3} M GA. The corresponding voltammograms are as shown in Fig. 5(a). E_{pa} of GA shifts in the positive direction with an increase in scan rate. The I_{pa} of GA was found to vary linearly with the square root of scan rate as depicted

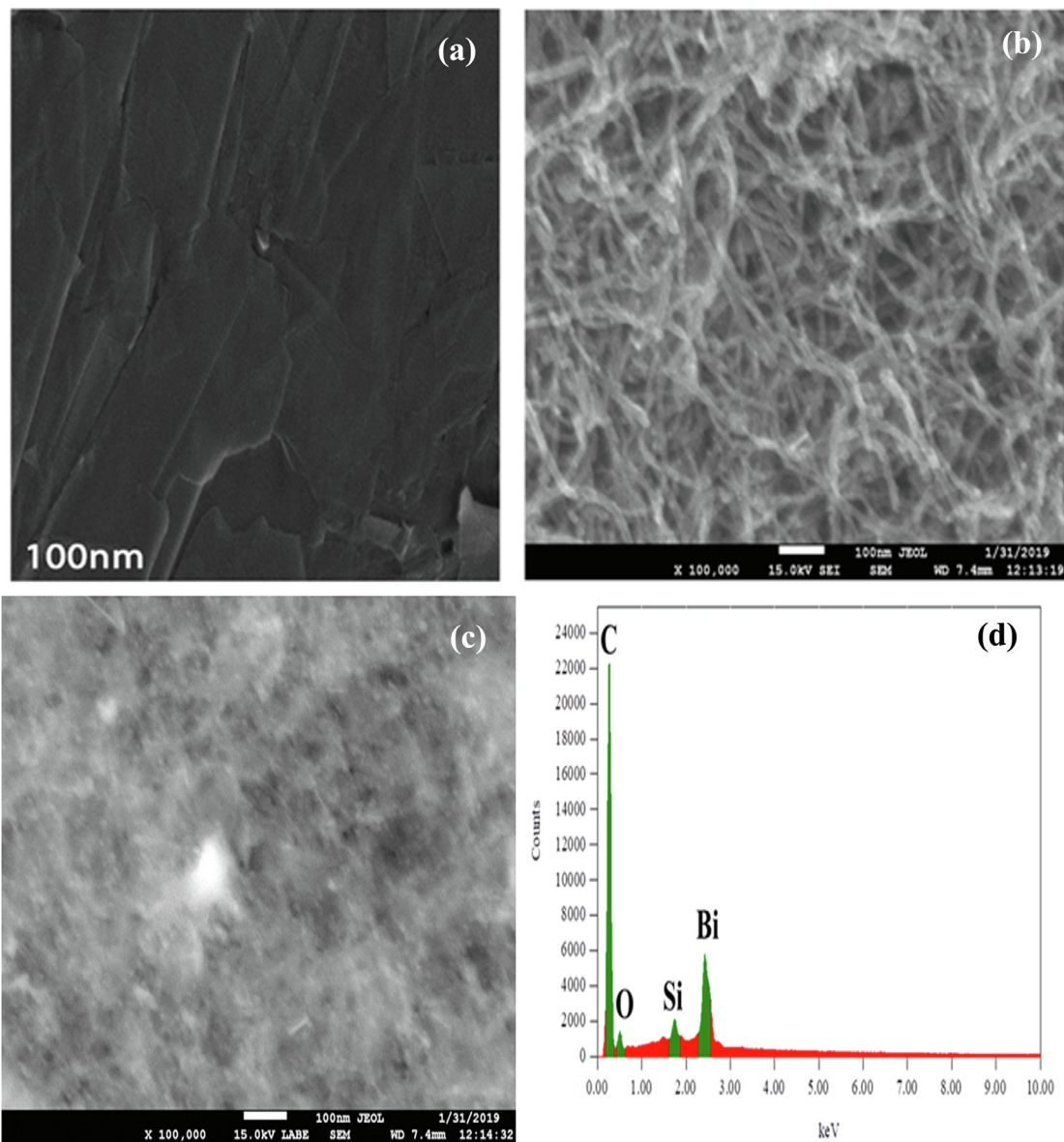


Fig. 2. FE-SEM images of (a) CPE, (b) Bi-MWCNT/MCPE (SEI mode), (c) Bi-MWCNT/MCPE (LBE mode) and (d) EDX of Bi-MWCNT/MCPE.

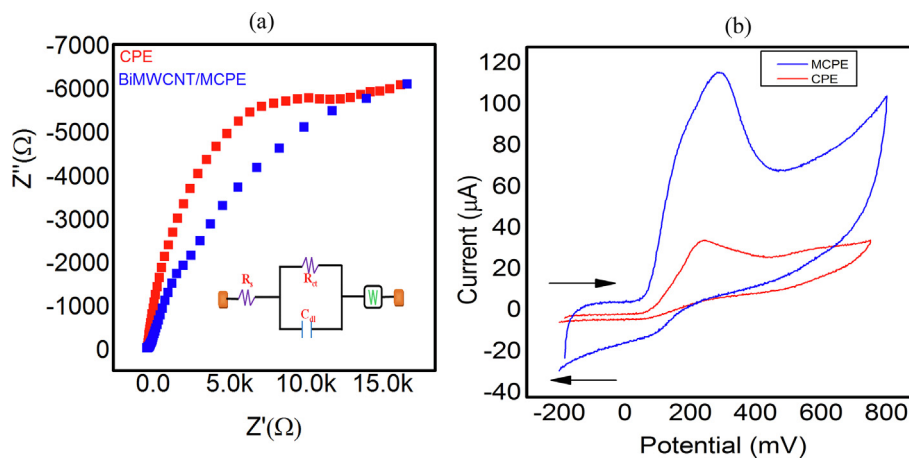


Fig. 3. 1×10^{-3} M GA in 0.1 M phosphate buffer solution of pH 7.0 (a) Nyquist plot. Inset: Randles circuit. (b) Cyclic voltammograms of GA at CPE and Bi-MWCNT/MCPE with a scan rate of 50 mV s⁻¹.

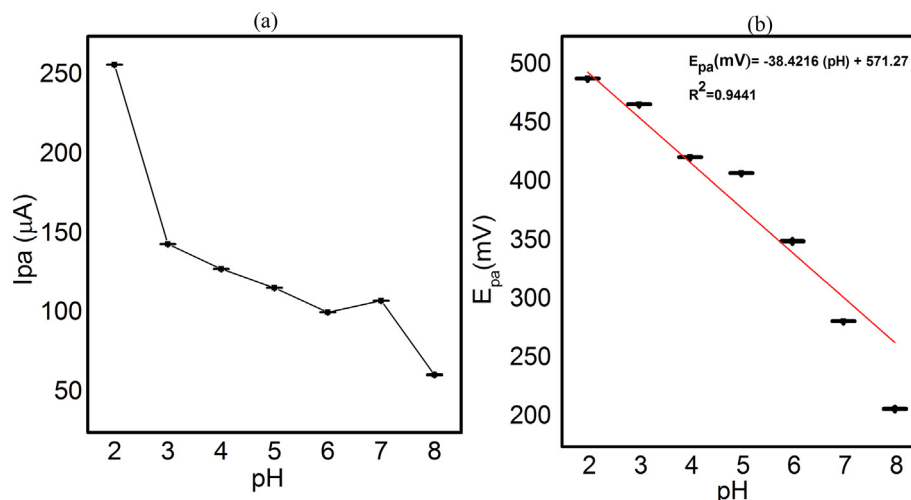


Fig. 4. (a) Effect of solution pH on 1×10^{-3} M GA oxidation current at Bi-MWCNT/MCPE (scan of 50 mV s^{-1}) (b) oxidation peak potential versus pH.

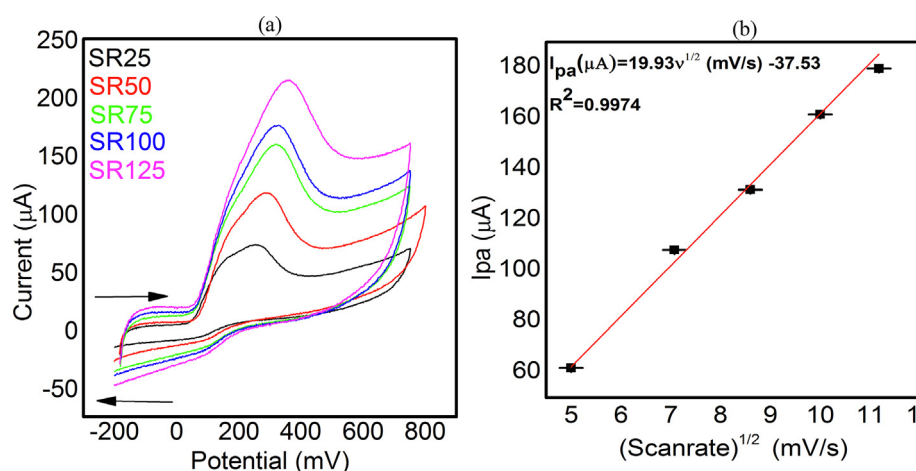


Fig. 5. (a) CVs of 1×10^{-3} M GA at varying scan rates from 25 to 125 mV s^{-1} . (b) Linear plot of $(\text{scanrate})^{1/2}$ vs I_{pa} .

in Fig. 5(b). The corresponding linear regression equation was: $I_{pa} = -37.53 + 19.93 v^{1/2} (\text{mV s}^{-1})$ with $R^2 = 0.9974$. Such a behavior indicates that the electrochemical oxidation of GA at Bi-MWCNTs/MCPE is a diffusion controlled process.

3.8. Determination of limit of detection and calibration curve

To determine the sensitivity of Bi-MWCNT/MCPE, amperometric technique was chosen because of its high sensitivity and better resolution as compared to CV. The amperometric technique was performed under hydrodynamic conditions. To obtain better detection limits, parameters such as pulse interval, pulse width and pulse amplitude were optimized. The amperometric responses of GA were taken in 0.1 M PBS of pH 7.0 at Bi-MWCNT/MCPE whose potential was set to 300.0 mV versus SCE. Aliquots of GA were spiked into the buffer solution under stirred conditions and Bi-MWCNT/MCPE gave quick responses. The response attained stability within 6.0 s.

An Amperogram of well-defined steps confirms the ability of the electrode to detect that particular concentration as shown in Fig. 6. The amperometric current response of GA was found to be linear in the concentration range $1.0\text{--}100.0 \mu\text{M}$ as shown in Fig. 6(c). The corresponding linear regression equations were

$I_{pa} = -0.0208 + 0.4399C (\mu\text{M})$ with $R^2 = 0.9982$. Then standard deviation was calculated for concordant blank reading. Then the LOD was calculated using the formula [42]:

$$\text{LOD} = 3.3 \times s_d / \text{slope from the regression line} \quad (2)$$

where s_d is the standard deviation of the regression line. The LOD for GA was found to be $1.6 \times 10^{-7} \text{ M}$ at a signal to noise ratio of 3. The developed sensor was found to have a wide linear dynamic range and we successfully achieved low detection limit for GA quantification.

3.9. Interference study

To check for the selectivity of our proposed electrochemical sensor, interference study was conducted. We chose AA as the interferent since it is found commonly in real matrices such as food items and plant kingdom. Amperometric technique was employed to check the anti-interferent property of our electrode. The responses of GA remained intact in presence of $1.0 \mu\text{M}$ AA as shown in Fig. S3 (Supplementary information). Since we observed no step for AA in the amperometric response, this authenticated the anti-interferent property of our sensor.

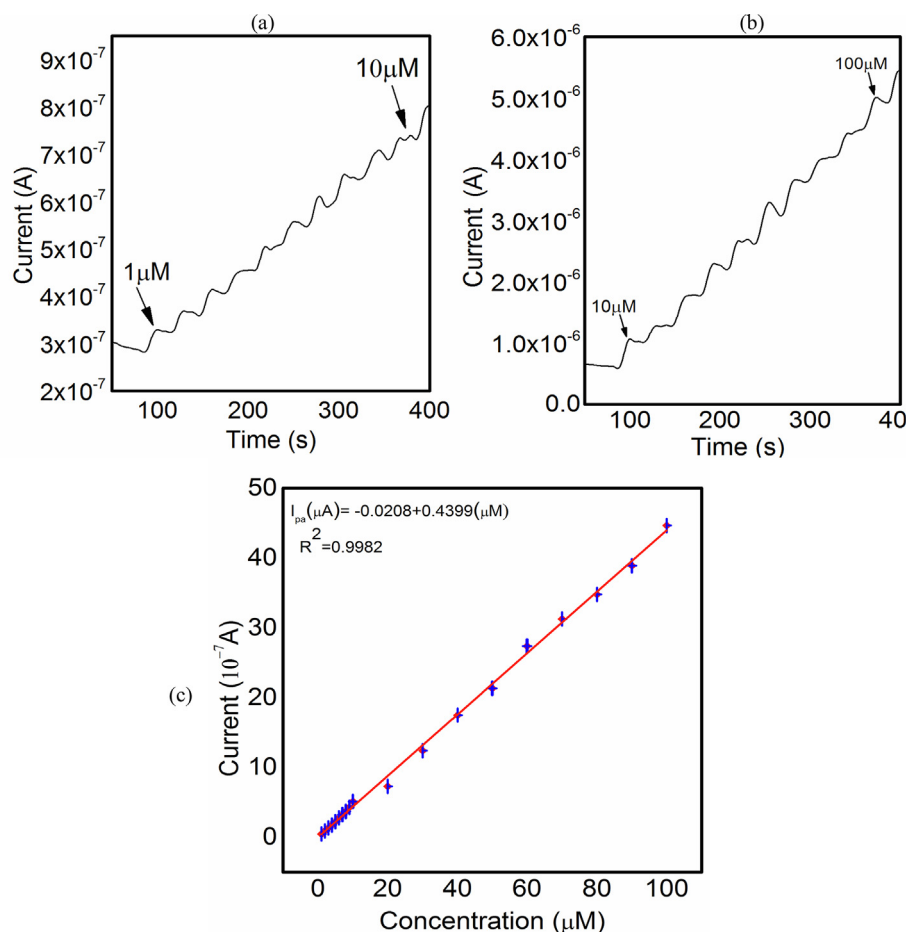


Fig. 6. Amperometric plots of (a) 1.0–10.0 μM . (b) 10.0–100.0 μM solutions of GA in PBS buffer at pH 7.0. (c) Calibration curve for 1.0–100.0 μM GA in PBS buffer at pH 7.0

3.10. Comparison of analytical performance of present sensor with other sensors reported in the literature

The preparation of 3D amorphous carbon involves sophistication and a lot of time [44]. Though the SCPE/PME [43] electrode works at neutral pH and has a wide linear dynamic range it suffers single use. $\text{ZrO}_2\text{-ChCl-AuNPs/CPE}$ [46] involves double modification and more over the work was done in acidic pH. The other sensors using glassy carbon electrodes have to undergo a rigorous pretreatment prior to the preparation in the case of PEP/GCE [48], and PEI-rGO/GCE [44]. AgNPs/Delph/GCE [49], AuMCs/SF-

GR/GCE [50] involve a tedious preparation procedure and the use of Ag, Au and the modifiers making it an expensive sensor. The CCE/mRGO [45] requires a week of drying time making it tedious in its preparation and requires acidic medium for detection. PDDA-GR-Pt/GCE [51] surface from intricate procedural preparation requiring pretreatment and suffers from poor linear dynamic range and requiring acid medium for detection. WCrGO/GCE, TNrGO/GCE [52] involves expensive materials as modifiers with poor dynamic range and detection limit. Our developed sensor has a relatively easy method of modification, inexpensiveness, no pretreatment, good reproducibility, sensitivity, selectivity, stabil-

Table 1
Comparison of present work with other electrodes reported in literature.

Electrode	pH	Linear dynamic range (μM)	Detection limit (μM)	Technique used	References
SPCE*/PME	7.0	1.0–1000.0	0.21	FIA	[43]
3D-porous amorphous carbon	4.0	1×10^{-7} – 1.5×10^{-5}	4.3×10^{-7}	DPV	[44]
CCE/mRGO	2.0	0.51–46.40	0.0867	SWV	[45]
$\text{ZrO}_2\text{-ChCl-AuNPs/CPE}$	3.0	0.22–55	0.025	DPV	[46]
PEI-rGO/GCE	2.0	1.0–100.0	0.7	DPV	[47]
PEP/GCE	7.0	1.0–20.0	0.663	ASV	[48]
AgNPs/Delph/GCE	7.0	8.68–625.80	0.28	AMP	[49]
AuMCs/SF-GR/GCE	4.0	0.05–8.0	0.01	DPV	[50]
PDDA-GR-Pt/GCE	2.5	0.03–1.0	0.007	SWV	[51]
WCrGO/GCE TNrGO/GCE	0.1 M H_2SO_4	10.0–100.0	3.1	DPV	[52]
		4.4–76	1.1		
Bi-MWCNT/MCPE	7.0	1.0–100.0	0.16	AMP	Present work

Abbreviations: SPCE*/PME = Screen printed carbon electrode/Polymelamine, CCE/mRGO = Carbon ceramic electrode, $\text{ZrO}_2\text{-ChCl-AuNPs}$ = zirconia-cholinechloride-gold nanoparticles, PEI-rGO = polyethyleneimine-functionalized graphene oxide, PEP = polyepinephrine, AgNPs/Delph = silver nanoparticle/delphinidin, AuMCs/SF-GR = gold microclusters/sulfonate functionalized graphene, PDDA-GR-Pt = Pt nanoparticle decorated polyelectrolyte functionalized graphene modified electrode, WCrGO = wolfram carbide-doped reduced graphene oxide, TNrGO = titanium nitride-doped reduced graphene oxide, CPE = carbon paste electrode, GCE = glassy carbon electrode, FIA = Flow injection analysis, DPV = differential pulse voltammetry, SWV = square wave voltammetry, ASV = Anodic stripping voltammetry, AMP = amperometry.

Table 2

Results of real sample analysis at Bi-MWCNT/MCPE.

Sample	GA added (μL)	GA found (μL)	GA recovery (%)
Clove Extract	15	15.6 ± 0.10	104.0
	20	20.5 ± 0.10	102.5
Green Tea Extract	15	15.1 ± 0.01	100.4
	20	19.9 ± 0.50	99.5

ity, wide linear dynamic range, amenability to be used at neutral pH and better detection limit makes it superior and more convenient for use a sensor as compared to many modified electrodes reported in the literature (as indicated in Table 1) for the detection of GA.

3.11. Real sample analysis

The analytical utility of the developed sensor was evaluated by employing it in the determination of GA in clove and green tea by standard addition method. The estimation of GA was done by recovery studies in both the samples. An appropriate quantity of clove extract, whose concentration fell within the working concentration range, was directly added to 0.1 M PBS of pH 7.0 under stirred condition and the amperometric response was recorded at Bi-MWCNT/MCPE. Similarly green tea extract was diluted with PBS (7.0) and this was followed by it being spiked with standard solutions of GA. The corresponding amperometric responses were recorded. Quantitative recoveries in the acceptable range were obtained for GA; both in clove extract and green tea sample at Bi-MWCNT/MCPE. The results were as tabulated in Table 2. Thus these observations ascertained the practical utility of Bi-MWCNT/MCPE as a reliable probe for the analysis of GA in real samples.

3.12. Stability of the electrode

A series of five modified electrodes were prepared in the same manner and the CV responses of 1×10^{-3} M GA was recorded consequently. A relative standard deviation of 2.21% observed for these measurements indicates an excellent reproducibility of Bi-MWCNT/MCPE. Next, to examine the stability of our electrode, an amperometric response was taken for 1×10^{-6} M GA at Bi-MWCNT/MCPE. A constant potential of 300 mV was applied into the above mentioned solution over a period of half an hour is displayed in Fig. S4 (Supplementary information). The amperometric response remained constant throughout the experiment. This attests the proposed sensor's stability and implies that it does not undergo any surface fouling.

4. Conclusion

A sensitive, selective and cost effective sensor for the determination of GA in solution at physiological pH was developed. The Bi-MWCNT/MCPE showed excellent activity for GA and hence an enhancement in current compared to bare CPE was observed. The current enhancement was found to be three folds higher compared to the bare CPE. Voltammetry techniques were successfully employed which gave superior analytical results. Based on the study, optimization of various parameters like pH, scan rate, casting volume etc was conducted. Trace level detection of GA was performed using amperometry. The developed sensor has a wide linear dynamic range with the detection limit of 1.6×10^{-7} M. The developed sensor can be successfully applied for real sample analysis thereby making it a potential candidate to be used as a sensor for the detection of GA in various real samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mset.2019.10.001>.

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